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MICROSTRUCTURE DEVELOPMENT IN POLYMERS.(U)  
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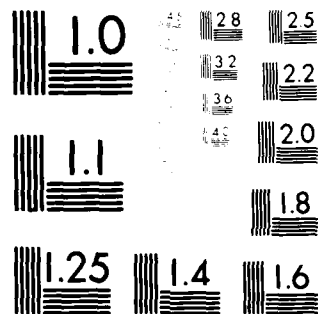
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MICROSTRUCTURE DEVELOPMENT IN POLYMERS

Final Report

Jerold M. Schultz

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  The development of microstructure in unperturbed and in deformed polymer melts and solids has been studied. In much of the work the Oak Ridge 10-Meter SAXS Instrument has been used. For undeformed systems, results relate to the geometry and phase properties of the crystallizing material. For deformed systems, a complex sequence of events is described: basically the rapid formation of fibrillar, imperfect crystals and their subsequent internal		

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20. ABSTRACT CONTINUED

rearrangements. Mechanical property development is related to the observed changes.

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## FINAL REPORT

The problem area attacked was that of microstructure development in polymers. A number of systems were studied. These systems can be divided into two groups: transformations in quiescent material and transformations in systems undergoing simultaneous deformation and transformation. The two areas are treated separately below.

### A. Quiescent Transformations

In one part of this work, the Oak Ridge National Laboratory (ORNL) 10-Meter Small-Angle X-ray Scattering (SAXS) Instrument was used to follow in situ the development of microstructure during the crystallization of polyethylene from its melt. The ORNL instrument is of high speed and resolution. This work lead to the following conclusions:

- Crystallization occurs through the growth of plate-like crystals whose thickness is invariant through the transformation.<sup>1</sup>
- Final stages of crystallization take place through the filling of included "gaps" and the cannibalization of smaller crystals by larger.<sup>2</sup>
- The yield stress of melt-crystallized material depends on the crystallization time, apparently reflecting changes in the density of linkage connecting adjacent crystallites.<sup>2</sup>
- The macroscopic kinetic behavior can be followed by measurement of integrated SAXS measurements. Avrami's Law is found to hold by such measurements.<sup>3</sup>
- Analysis of absolute integrated intensities provides a quantitative measure of the density of the non-crystalline phase. This amorphous density, in all

cases studied, lies on the extrapolation to the melt density.<sup>2,3</sup>

In another project, room temperature physical aging of polypropylene was studied, using several methods.<sup>4,5</sup> New methods<sup>4</sup> were used to follow the elastic modulus and density to aging times much lower than those previously reported. Analysis of infrared, dynamical mechanical loss, infrared absorption, and x-ray small- and wide-angle scattering showed that the aging process occurs entirely in the non-crystalline phase. This phase densifies with no concomitant gross chain conformational change.<sup>5</sup>

A small project to explain the microstructural basis of a large temperature dependence of piezoelectricity in poly(vinylidene fluoride) was also completed. This work showed that temperature affects microstructure in this operating range by the reversible melting of crystallites.<sup>6</sup>

#### B. Transformations Under High Deformation

In this area, three materials systems were studied. There were (a) the crystallization of thin polymer films drawn from the melt; (b) the transformation of melt-spun and annealed poly(ethylene terephthalate) (PET) fibers, and (c) the recrystallization of cold-drawn polypropylene (PP) sheet.

In (a) electron-transmissible films of PP<sup>7,8</sup>, polystyrene<sup>9</sup>, and poly(butene-1)<sup>10</sup> were formed by a laboratory-scale melt-drawing process. In the as-crystallized state, the films exhibit fibrillar crystals, aligned in the melt-

draw direction and embedded in a non-crystalline sea. Upon further treatment, the fibrillar entities develop a sinusoidal axial density fluctuation. The details of this density fluctuation and the kinetics of its formation are consistent with a spinodal model, in which non-kinked and kinked segments form a two-"component" alloy.

In (b), commercial spun PET fibers were heat treated isothermally for times as short as 35 msec.<sup>10</sup> The kinetics of the crystallization of this material are very rapid, with half-times ranging from <50 msec to some few seconds. It was found that fibrillar crystalline entities form at the shortest treatment times measurable. With longer treatments, a density modulation associated with increased crystallinity, develops axially in the fibrillar entities. Mechanical properties were followed and were found to vary continuously with the change in axial density modulation.

In (c), tensile bars of PP were drawn at room temperature and then subsequently heat-treated isothermally.<sup>11</sup> The results again showed a sinusoidal density modulation, whose details are consistent with a spinodal model. Mechanical property changes, however, followed kinetics which were faster than the observed microstructural change.

From these studies a conceptually new model for crystallization during deformation is developing. Important ingredients of the approach are the details of heat flow in the crystallizing system, the storage of a portion of the heat of fusion as lattice defects, and, finally, the rearrangement of those lattice defects by a spinodal mode.

Further work on transformations during the thermal processing of spun and cold-drawn Nylon 6.6 fiber is currently in progress.

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## List of Publications

### A. Published

1. J. M. Schultz, J. S. Lin, and R. W. Hendricks, "A Dynamic Study of the Crystallization of Polyethylene from the Melt," Journal of Applied Crystallography, 11, 551-557 (1978).
2. M. J. McCready, J. M. Schultz, J. S. Lin, and R. W. Hendricks, "Effect of Crystallization Time on the Properties of Melt-Crystallized Linear Polyethylene," Journal of Polymer Science, Polymer Physics Edition, 17, 725-740 (1979).
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4. J. M. Petermann, R. M. Gohil, J. M. Schultz, R. W. Hendricks, and J. S. Lin, "Small-Angle X-ray Scattering from Polybutene-1 Films Crystallized from a Highly Extended Melt," Journal of Materials Science, 16, 265-268 (1981).
5. J. M. Schultz, J. S. Lin, R. W. Hendricks, J. Petermann, and R. M. Gohil, "Annealing of Polypropylene Films Crystallized from a Highly Extended Melt," Journal of Polymer Science, Polymer Physics Edition, 19, 609-621 (1981).

### B. In Press

1. M. K. Agarwal and J. M. Schultz, "The Physical Aging of Isotactic Polypropylene," Polymer Engineering and Science.
2. J. S. Baum and J. M. Schultz, "Rapid Measurement of Elastic Modulus and Density in Polypropylene Sheet During Aging," Journal of Applied Polymer Science.
3. Suzanne Babajko and J. M. Schultz, "Kinetics of Microstructure Rearrangement During Annealing of Cold-Drawn Isotactic Polypropylene," Journal of Polymer Science, Polymer Physics Edition.

List of Publications

B. In Press (Cont'd)

4. J. Petermann, J. M. Schultz, R. M. Gohil, R. W. Hendricks, and J. S. Lin, "The Kinetics of Defect Clustering in Fibrillar Polypropylene Crystals," Polymer.

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